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ORGANOFUNCTIONAL PHOSPHAZENES AND ORGANOFUNCTIONAL  
PHOSPHAZENE POLYMERS(U) VERMONT UNIV BURLINGTON DEPT OF  
CHEMISTRY C W ALLEN 19 FEB 86 TR-17 N00014-77-C-0605

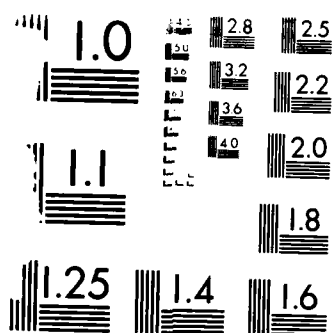
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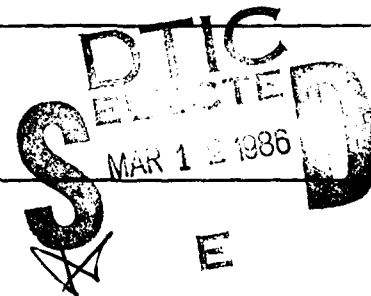
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The report provides a brief outline of the approaches used to build traditional polymers with cyclophosphazene moieties as substituents. The physical and chemical properties, including flame retardancy, of these materials are noted.			



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Final Report, 1985

to

The Office of Naval Research

1. Title: Organofunctional Phosphazenes and Organofunctional Phosphazene Polymers

NR-Number: 356-663

Contract Number: N001477C-0605

Principal Investigator: Christopher W. Allen

Institution: The University of Vermont  
Burlington, Vermont 05405

2. Brief Description of the Project

The basic strategy of this project has been the incorporation of various cyclophosphazenes, and thus certain of their useful properties, into tradition, commercially important organic polymers (technical reports 3,13). This goal has been realized by the synthesis of cyclophosphazenes with substituents which can enter into polymerization reactions (technical reports 1,8,9,11,12,14,15). The specific mode of polymerization has involved radical addition copolymerization of the alkenyl (technical reports 2,3,8,13) or alkynyl (technical report 13) phosphazene with common organic comonomers such as styrenes, methyl methacrylate, etc. The resulting copolymers resemble the parent organic polymer except for a broader range of solubility and the incorporation of significant flame retardant behavior (technical reports 2,3). Molecular weights (by several methods), molecular weight distributions and thermal analysis behavior have been measured for all new polymers. Evidence has been obtained to indicate that the phosphazene is involved in the termination step (technical reports 2,13). A systematic examination of the effect of structure modifications on the electronic structure and reactivity of the olefin center was carried out. Variations include effect of olefin substituents (technical reports 1,12), the introduction of an insulating function, such as oxygen atoms or phenyl groups, between the olefin and the phosphazene (technical reports 9,11,15) and changing phosphazene substituents (technical reports 11,13,15). The effects of these variations were quantitatively assessed by calculation of reactivity ratios and Alfrey-Price Q,e parameters (technical report 13). Evidence of penultimate effects has been obtained in the para- $\alpha$ -methystyrylpentafluorophosphazene/methyl methacrylate copolymerization. Two monomers,  $N_3P_3Cl_5OCH=CH_2$  (technical report 11) and  $N_3P_3F_5C_6H_4CH=CH_2$ , were developed for homopolymerization studies. These unique homopolymers are the first representatives of a new class of materials having an organic backbone and a highly functionalized inorganic surface (technical report 13). Thermal decomposition of these materials leads to moderate yields of solids which are involatile up to 900 to 1100 °C.

### 3. Technical Reports

- No. 1    "Organosubstituted Phosphazenes. X. Reactions of Hexafluorocyclotriphosphazene with Propenyl Lithium Reagents" (J.G. Dupont and C.W. Allen, Inorg. Chem., 17, 3093 (1978)).
- No. 2    "Organophosphazenes. XI. Copolymers Derived from 2-[propenyl]pentafluorocyclotriphosphazene and Vinyl Benzyl Chloride or Styrene (J.G. Dupont and C.W. Allen, Macromolecules, 12, 169 (1979)).
- No. 3    "Novel Propenylfluorophosphazene-Styrene Copolymers" (C.W. Allen and J.G. Dupont, Ind. Eng. Chem. Product R D, 18, 80 (1979)).
- No. 4    "Organophosphazenes. XII. He(I) Photoelectron Spectra of Selected Phenyl- and p-N,N-Dimethylaminofluorocyclotriphosphazenes" (C.W. Allen and J.C. Green, Inorg. Chem., 19, 1719 (1980)).
- No. 5    "Organophosphazenes. XIII. Reactions of Hexfluorocyclotriphosphazene with p-N,N-Dimethylaminophenyl Lithium and Gregnard Reagents" (C.W. Allen and P.L. Toch, Inorg. Chem., 20, 8 (1981)).
- No. 6    "Organophosphazenes. XIV. Para Substituted Aryl and Mixed Para Substituted Aryl and Mixed Para Substituted Aryl/Phenyl Fluorocyclotriphosphazenes" (C.W. Allen, G.E. Brunst and M.E. Perlman (Inorg. Chimica Acta, 41, 265 (1980)).
- No. 7    "Organofluorophosphazenes: A Short Review" (C.W. Allen, Ind. Eng. Chem. Product R D, 20, 77 (1981)).
- No. 8    "Alkenylfluorocyclotriphosphazenes" (C.W. Allen, R.P. Bright and K. Ramachandran, ACS Sympsoium Series: PHosphorus Chemistry, 171, 321 (1981).
- No. 9    "A Reinvestigation of the Reactions of Enaolate Anions with Cyclotriphosphazenes" (C.W. Allen, K. Ramachandran, R.P. Bright and J.C. Shaw, (Inorg. Chim. Acta, 64, L109 (1982)).
- No. 10    "Organophosphazenes. 15. Reactions of Hexafluorocyclotriphosphazene with Tert- and n-Butyl Lithium Reagents (K. Ramachandran and C.W. Allen, J. Amer. Chem. Soc., 104, 2396 (1982)).
- No. 11    "(Vinyloxy)chlorocyclotriphosphazenes" (K. Ramachandran and C.W. Allen, Inorg. Chem., 22, 1445 (1983)).
- No. 12    "Organophosphazenes. 16. Synthesis and Reactions of (1-Alkoxyvinyl)fluorocyclotriphosphazenes" (C.W. Allen and R.P. Bright, Inorg. Chem., 22, 1291 (1983)).
- No. 13    "Organofunctional Phosphazenes and Organofunctional PHosphazene Polymers (C.W. Allen, J. Polym. Sci., Polym. Sym., 70, 79 (1983).

- No. 14 "Organophosphazenes. 17. The Synthesis of Trimethylsilylacetylene and Terminal Acetylene Derivatives of Hexafluorocyclotriphosphazene" (C.W. Allen, J.L. Desorcie and K. Ramachandran, J.C.S. Dalton, 2843 (1984).
- No. 15 "(Vinylxy)fluorocyclotriphosphazenes" (C.W. Allen and R.P. Bright, Inorg. Chim. Acta., 99, 107 (1985).
- No. 16 "Organophosphazenes. 18. Friedel-Crafts PHenylation Reactions of Alkyl and Dimethylamino Fluorocyclotriphosphazenes" (C.W. Allen, S. Bedell, W.T. Pennington and A.W. Cordes, Inorg. Chem., 24, 1653 (1985).

4. Students Supported on this Contract

A. Postdoctoral

Dr. Kolikara Ramachandran

B. Graduate Students

1. Dr. John Dupont (Ph.D. 1978)
2. Dr. Randall Bright (Ph.D. 1983)
3. Dr. Jon Shaw (Ph.D. 1985)
4. Mr. Douglas Brown (current Ph.D. student)
5. Ms. Pauline Malik (current Ph.D. student)
6. Ms. Lydia McNally (current Ph.D. student)

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